

# **THERMOGRAVIMETRIC/MASS SPECTROMETRIC (TG/MS) CHARACTERIZATION OF TONER PARTICLES FROM PHOTOCOPIED WASTEPAPER AND THE IMPACT OF THESE FEATURES ON FLOTATION DEINKING**

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## **ABSTRACT**

Flotation deinking of photocopies from office waste is known to be much more difficult than the flotation deinking of newsprint. In this regard, research has been undertaken to better understand the phenomena which account for the poor efficiency in the flotation deinking of such office waste. During the photocopying process, toner particles, mainly consisting of styrene-acrylate copolymer (>85%), are photoelectrically attached to the cellulose fiber and heated to bond the toner particles to the paper. Even with the short time of exposure to heat, light, and oxygen, it is expected that surface styrene groups undergo oxidation and polymerization with the subsequent formation of peroxide bonds. Thermogravimetry/mass spectrometry (TG/MS) results show that the decomposition temperatures of monomer, dimer and trimer styrenes and styrene-acrylate present in the toner particles have been increased by about 10 to 30 °C after photocopying, and that their decomposition activation energies have been increased by about 7 to 20 kcal/mol. Correspondingly, it was found that volatile release was diminished, that thermal stability of toner residue increased slightly, and that the phase change (softening) around 72 °C, which is below the printing temperature, disappeared. On the other hand, the acrylate component of the toner which contains the oxygen-functional groups (-OH and -O-), was found to be relatively more stable during the photocopying process and this

component of the toner was not affected. It appears that the strong bond of the toner particles with the cellulose fibers, the polymerization (fusion), and the oxidation of the styrene, which creates a greater polarity at the toner particle surface, accounts for the difficulty in making more efficient flotation deinking separations in the recycle of office waste containing photocopies.

## **INTRODUCTION**

In the U.S. approximately 50% of municipal-solid-waste (MSW) is made up of paper and related fiber products, which has a great impact on environmental, economic and energy issues.<sup>[1-8]</sup> Therefore, legislation in many states has focussed on recycling.<sup>[1]</sup> Wastepaper recycling is now being practiced in many urban areas and is becoming an increasingly important industry and a world wide market has been established.<sup>[1-4,9]</sup> Technology for deinking and cleaning of the cellulose fiber plays an important role in the wastepaper recycle process.<sup>[10]</sup>

Paper is a felted sheet of cellulose fibers formed during the papermaking process. The cellulose fibers have the basic structure of cellulose (poly(1→4)-β-D-glucopyranose) and the conformation of the glucopyranose ring is in the characteristic chair form.<sup>[11]</sup> Because of its large content of oxygen-functional groups (mostly -OH and -O- linkages) cellulose exhibits a distinct hydrophilic character. On the other hand, the surface characteristics of ink depend on composition and the nature of their reaction with the cellulose fibers to form print and images. Inks consist of four major compounds: pigments (color dye or carbon black), binders (polymers or oil), carriers, and small amount of additives, and basically tend to be hydrophobic. Therefore, the separation of ink particles from wastepaper pulp by froth flotation should be a reasonable processing strategy.<sup>[11-13]</sup> Air and chemicals are added to the suspension, ink particles attach to the air bubbles, collect in a froth, and hence are separated from the hydrophilic cellulose fiber.<sup>[14,15]</sup>

Many research efforts (mostly in Japan and Germany) have been made during the last decade to improve flotation deinking for wastepaper recycle and some significant progress has been made,<sup>[1,12,16-22]</sup> so much so that flotation has become the predominant process for deinking of wastepaper in Europe and Japan.<sup>[11]</sup> U.S. flotation deinking technology has lagged behind that of Japan and Europe until recently.<sup>[1,9,10,23-24]</sup> For example, highly efficient flotation deinking of newsprint wastes has been achieved at the University of Utah using the high specific capacity air sparged hydrocyclone (ASH).<sup>[12,16,17]</sup> Under appropriate control, a clean fiber product with about 7 points

brightness gain can be obtained at a yield of greater than 92% by single-stage ASH flotation of a waste newspaper stock.<sup>[12,16]</sup>

In the case of photocopied office waste, where the photocopying ink is photothermally fused and bonded to the cellulose fibers, flotation deinking has been much less successful when compared to the flotation deinking of waste newsprint.<sup>[25-27]</sup> Further fundamental studies are needed for a better understanding of the surface chemical reactions and changes in photocopying inks during the printing process so as to optimize the flotation deinking process for efficient recycle of this material.

## EXPERIMENTAL

Thermogravimetry (TG) and mass spectrometry (MS) systems have been broadly used for the study of cellulose and other polymers.<sup>[28-32]</sup> However, since the mass spectrometer is operated in the high vacuum ( $10^{-6}$  torr), most thermogravimetry/mass spectrometry systems on the market are either coupled by a capillary transfer line (usually a gas chromatographic column) to transfer the sample vapor and reduce the pressure<sup>[29-31]</sup> or by placing the thermogravimeter in the mass spectrometric high vacuum chamber.<sup>[33]</sup> In the first case, the long transfer line (2 ~ 30 m at about 0.25 mm i.d.) results in a long vapor sample residence time (0.5 ~ 15 min) from the reactor (TG) to the detector (MS) so that secondary reactions and sample condensation are very difficult or impossible to avoid. In the latter case, since the sample needs to be placed in the high vacuum chamber, some light volatile materials will escape from the sample before the experiment is initiated. Therefore, in both cases, accurate analysis, specifically for a small changes in surface state is difficult to be achieved. Recently, a novel atmospheric and short residence time (< 2 seconds) thermogravimetry/mass spectrometry (TG/MS) system was developed in the University of Utah.<sup>[34,35]</sup> The results from this research represent the first application of the short residence time thermogravimetry/mass spectrometry system for the characterization of toner particles from photocopied wastepaper.

### Materials

A photocopying toner (xerox dry ink plus 5052/1050, Xerox Corporation), the ingredients listed in Table 1, and white photocopying paper (xerox 4200, Xerox Corporation) were purchased and used for all characterization studies.

Photocopying wastes were made by using an Xerox 5052 copying machine (series 15P355826, Xerox Corporation) and the used (oxidized) toner powders were collected from the

machine's discard bottle.

## Methods

The TG/MS system shown in Figure 1, consisting of a Perkin-Elmer TFS-2 microbalance (sensitivity 0.1  $\mu$ g, accuracy 0.1%) and a Perkin-Elmer 7 series high temperature furnace was operated at the heating rate of 25 K/min up to temperature of 800 C. An Extrel EL 1000 quadrupole mass filter operating at 12 eV electron energy and a Teknivent Vector 2.2 interface combined with a PC based data system operating at scanning rates of 2.5 spectra/scan covering the 10-600 amu range.

Fifty mg aliquot of sample of paper-and-inks were loaded into a regular platinum crucible, and placed in the TG furnace where pyrolysis was performed in helium at atmospheric pressure. A 100 ml/min of helium was introduced through the top (95%) and bottom (15%) of the TG furnace. Between TG and mass spectrometer a special interface similar to an arrangement first described by Emminger and Kaisersberg<sup>[36]</sup>, and consisting of concentric outer (15 mm i.d.) and inner (3 mm i.d.) quartz tubes is used to reduce the pressure and transfer the vapor products. A countercurrent helium flow acts to direct the evolved gas and descend flows towards 80  $\mu$ m dia orifices of the quartz tubes. All of the sample vapors are drawn through the outer orifice and about 5% of the sample vapor is drawn through the inner orifice into the MS ion source region ( $10^{-6}$  torr). The short distances between sample holder and vapor sampling inlet (< 2 cm) and between inlet and MS ion source (< 15 cm) ensure vapor product response times < 2 seconds (Fig.2), which minimizes secondary reactions.

DSC experiments were performed in a Perkin-Elmer 7 Differential Scanning Calorimeter under the experimental conditions of the ambient nitrogen atmosphere at the flow rate of 20 ml/min and the temperature program at the heating rate of 20 K/min. 10 mg of sample was used for each test.

## RESULTS AND DISCUSSION

### Thermal Decomposition Reactions

Paper consists mainly of cellulose fibers, which have the basic structure of poly(1 $\rightarrow$ 4)- $\beta$ -D-glucopyranose and the conformation of the glucopyranose ring is in the characteristic chair form. Its thermal decomposition proceeds essentially through two types of reaction.<sup>[28]</sup> At lower temperatures, i.e. below 300 °C, there is a gradual degradation which involves dehydration, rearrangement, formation of carboxyl and carbonyl groups, evolution of carbon dioxide and carbon

monoxide and formation of carbonaceous char. At higher temperatures, rapid volatilization accompanied by the formation of intractable tars and carbonaceous residue occurs. The major product in the tar is laevoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose).<sup>[37,38]</sup> Therefore, at ambient helium pressure, the thermal decomposition of paper fiber actually starts about 270 °C and is finished at about 400 °C (Fig.3). The main decomposition products are dianhydro- $\alpha$ -D-glucopyranose (m/z 144), 5-hydroxy-methylfurfural and laevoglucosenone (m/z 126), furfuryl alcohol (m/z 98), propionic acid (m/z 73), methylvinylketone (m/z 70), acetic acid (m/z 60), acetone and glyoxal (m/z 57), acetaldehyde (m/z 43) and formaldehyde (m/z 31), as shown in Fig.4a. All of these compounds contain =O, -O-, and/or -OH functional groups, which accounts for the fibers extensive hydration. This hydrophilic character explains why cellulose fibers generally remain dispersed in suspension during flotation.

The toner particles used in this study (xerox dry ink plus 5052/1050) are dry, consist of carbon black (10 ~ 15 %) as pigment in a thermoplastic resin styrene-acrylate copolymer binder (85 ~ 90%) and a small amount of zinc stearate (<1%) as a dry lubricant. In the temperature region of 350 ~ 460 °C (Fig.3), the styrene-acrylate copolymer decomposed into different daughter compounds, such as styrene (m/z 104),  $\alpha$ -methylstyrene (m/z 118), toluene (m/z 92), methylacrylate (m/z 87), benzene (m/z 78), acrylic aldehyde (m/z 56) and dimer and trimer styrenes and acrylates (Fig.4b).

Since paper fiber and photocopying toner particles have different decomposition temperature regions, the photocopied paper has two peaks in its thermogravimetry/mass spectrometry (TG/MS) decomposition curves of total ion chromatogram (TIC), (Figs.2 and 3). From the discussion above, the two temperature regions for paper fiber and photocopying toner decompositions overlap each other by about 50 ~ 60 °C (Fig.3). So for these experimental conditions the two curves can not be totally separated in the TG/MS decomposition curves (Figs.2 and 3), which makes analysis difficult. However, according to the results shown in Fig. 4, the main decomposition products of the fiber and toner are significantly different. Thus, the photocopied paper can be examined with mass spectrometry by using the selected ion chromatogram (SIC) without the problem or complicated of overlap.

When making a photocopy, ink particles are photoelectrically injected on to the paper. Most of ink particles injected are bonded on the paper surface to form an image, but some drop into a waste bottle to be discarded. These ink particles collected in the waste bottle (later called oxidized ink) were collected for analyses by the TG/MS. The TIC results were

plotted with that of unused toner particles (later called fresh ink) in Figs.5a and 5b. It can be seen that the decomposition temperature of the oxidized ink was about 7 °C higher (Fig.5a), and the amount of decomposition was about 7% smaller (Fig.5b) compared to those of the fresh ink. Correspondingly, a small, but a significant, 1.3 % more residue was found by thermogravimetric analysis in the thermal decomposition temperature region (up to 550 °C, after that the char gasification will happen) for the oxidized ink (Fig. 6).

By considering the overall thermal decomposition, as used for polystyrene, copolystyrene and other polymers,<sup>[34,39-42]</sup> a first order kinetic model can be written as follows:

$$\frac{d}{dt} \left( \frac{\Delta P_t}{\Delta P_\infty} \right) = k_o \left( \frac{\Delta P_\infty - \Delta P_t}{\Delta P_\infty} \right) \cdot \exp \left( - \frac{E_a}{RT} \right) \quad (1)$$

where  $\Delta P_t$  and  $\Delta P_\infty$  are the decompositions of the polymer at time  $t$  and at the end of the reaction step, respectively,  $k_o$  is the rate constant at a very high temperature,  $E_a$  is the apparent activation energy,  $R$  is the ideal gas constant.

Eq. [1] can be rewritten by using Freeman and Carroll's method<sup>[43]</sup> with finite differences

$$\Delta \ln \frac{d\Delta P_t}{dt(\Delta P_\infty - \Delta P_t)} = - \frac{E_a}{R} \Delta \left( \frac{1}{T} \right) + \ln k_o \quad (2)$$

By using eq.[2], the data in Fig.5a were plotted in Fig. 7, where the  $k$  is  $d\Delta P_t / (\Delta P_\infty - \Delta P_t)$  since the same  $dt$  interval was taken. From the well fitted straight line, the apparent activation energy for the decomposition was calculated to be 40.8 kcal/mol for the fresh toner particles, which is similar to the values obtained for poly- $\alpha$ -acetoxystyrene (40 kcal/mol) by Sahraoui et al.<sup>[41]</sup> and for polystyrene (43 kcal/mol) by Boustier et al.<sup>[42]</sup> However, corresponding to its higher decomposition temperature, the apparent activation energy for the oxidized toner was 3 kcal/mol greater than that for the fresh toner.

The results of a differential scanning calorimeter (DSC) in Fig.8 show that the fresh photocopying toner particles start fusing at 67 °C and finish it at 75 °C, which has a maximum fusing temperature,  $T_{max}$ , at 72 °C. The fusing temperature shifts to higher temperature with a maximum fusing temperature of 73 °C for the particles collected from the waste bottle. When a fresh toner sample which has been run in the differential scanning calorimeter in the ambient nitrogen from 50 to 150 °C is rerun in the same condition for the second time, the endothermic fusing peak disappears (Fig.9). Since the

experiment was carried out in the inert atmosphere and the corresponding thermogravimetric results (Fig.2a) do not show any weight loss at the temperature of around 72 °C, the results in the Fig.4 are considered as that at the around temperature 72 °C, the photocopying toner particles are fused and polymerized, and because of the polymerization, the particles do not fuse at this temperature any more.

### Products from Styrene Decomposition

From literature [44,45], the main volatile products from the thermal decomposition of styrene-acrylonitrile copolymers and polystyrene are monomers, dimers and trimers. Therefore, the monomers, dimers and trimers of toner inks were used for further investigation, which shows that the monomer, dimer and trimer styrenes (styrene, diphenylbutene and triphenylhexene) from oxidized toner particles have the same higher decomposition temperature shift (8 °C) as the TIC curve did (Fig.10). When a toner particle was fused (bonded) to paper, it was exposed to heat, light, and oxygen (air) for a longer time and at a higher temperature when compared to a particle collected in the discard bottle. The fused particle undergoes stronger oxidation and polymerization (or called as modification). The decomposition curves for the monomer and dimer styrene of the bonded toner particles shifted further to even higher temperatures, 25 and 20 °C shift, respectively (Figs. 10a and 10b). (The decomposition peak of the styrene trimer in the bonded toner particle was too small to be plotted.) Correspondingly, Fig. 11 shows that as the molecular weight of the polystyrene increases, i.e. as polymerization progresses, the apparent activation energies of decomposition increase. For example, those of monomer, dimer and trimer styrene increased from 39 to 55 kcal/mol for the fresh toner, which behaves a chain-end decomposition reaction.<sup>[42]</sup> Further, as the molecular weights of the styrenes increase, the activation energies became more sensitive to thermal exposure, so that the apparent activation energies for monomer, dimer and trimer styrenes increased about 5.4, 7.1 and 12 kcal/mol when the oxidized toner was compared to the fresh toner, and the activation energies for monomer and dimer styrenes increase by 15 and 21 kcal/mol when the fused toner was compared to the fresh toner.

### Products from Acrylate Decomposition

On the other hand, the acrylate components in the toner which originally contain oxygen functional groups (-OH and -O-), are relatively more stable, the decomposition curves, such as acrylic aldehyde (m/z 56), methylacrylate (m/z 87), dimer and trimer acrylate (m/z 144 and 216) do not show the same temperature shift after the photocopying process (Fig.12).

The decomposition curves of the styrene-acrylate co-monomer in the toner show the similar shifts of the decomposition temperature (9 °C) and apparent activation energy (13 kcal/mol) to those of styrenes when compared the oxidized toner to the fresh toner (Figs.13 and 14). When the data presented in Fig.13 are plotted on an absolute intensity scale (Fig.15), it is evident that the amount of decomposed co-monomer styrene-acrylate was decreased after thermal exposure. In view of the foregoing, modification of the styrene-acrylate component should be expected to be mainly contributed to reaction of the styrene branches.

### Oxygen Containing Products from Thermal Decomposition

Toner thermal decomposition products from photocopied wastepaper were found to consist primarily of toluene, styrenes and acrylates. However, a small but significant amount of simple oxygen containing compounds were identified. These compounds are believed to form at the particle surface during the short exposure time for printing. The system background for most of these products ( $\text{O}_2$  m/z 32,  $\text{H}_2\text{O}$  m/z 18,  $\text{CO}$  m/z 28 and  $\text{CO}_2$  m/z 44) was relatively high even for experiments carried out in a high purity helium atmosphere. Further, according to Billiani et al<sup>[46]</sup> in the study of the styrene-maleic anhydride copolymer, the  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are released at a temperature 80 °C lower than the temperature for the decomposition of the backbone of copolymer, which means that their peaks would overlap with the peaks of the cellulose fiber. Therefore, it is difficult to observe the products directly by TG/MS. However, the spectra of the fused toner ink particles (Fig.16c) show that the  $\text{O}_2$ ,  $\text{CO}$  and  $\text{H}_2\text{O}$  significantly increase even though they may have some offset as a result of the fiber's decomposition. In order to compensate for variations in sample size and experimental conditions, an acrylate compound,  $\alpha$ -methylacrylate (m/z 87) was selected as an internal standard because of its stability during the photocopying process. The abundance of methylacrylate was measured against the abundance of  $\alpha$ -methylstyrene (m/z 118), although monomer styrene at m/z 104 has been preferable to use, it is the main decomposition product and its abundance was too high to see the tiny difference. The results show that as the extent of thermal exposure increases, the relative amount of  $\alpha$ -methylstyrene decrease (Table II and Fig. 16), which indicates that some of the styrenes on the toner particles' surface have been oxidized during the copying process. When styrene undergoes polymerization, one of the main degradation products of the polymer is toluene (m/z 92).<sup>[42,46]</sup> Therefore, the ratio of the abundances of the toluene and methylacrylate show that as the thermal exposure increase, the ratio increases (Table II and Fig. 16).

## Toner Reaction Phenomena during Printing

The results above illustrate that toner particles undergo some modest, but distinct, changes during the photocopying process. A latent image is formed on a charged photoconductive surface and transferred to paper. The charged surface receives light reflected off the document to be copied. The light reflected from the nonprinted areas causes the surface charge to dissipate, while other areas in the absence of light retain their charge. The surface is then exposed to toner particles of opposite charge, which adhere to the charged area, forming a visible image. Finally, the image is transferred to the paper and the toner particles are heated to 70 ~ 200 °C to fuse the styrene-acrylate and to bond the toner particles to the paper.<sup>[25]</sup> Even with the short time of exposure to heat, light, and oxygen (air), the styrene groups, especially the styrene groups at the particle surface, undergo oxidation and polymerization with the formation of peroxides.<sup>[40,44,47,48]</sup> Because of oxidation and polymerization, the styrene double bonds break into more stable single bonds, which have a higher activation energy for the thermal decomposition reaction.<sup>[42]</sup>

## Deinking Flotation

The efficiency of deinking flotation significantly depends upon the surface characteristics of the printed ink particles and the cellulose fibers. Recycle of newsprint wastes is typically accomplished by flotation deinking techniques, most recently at high efficiency and high capacity with air-sparged hydrocyclone (ASH) technology.<sup>[12,16,17]</sup> But according to our own work and results reported in the literature<sup>[26]</sup>, both conventional and air-sparged hydrocyclone flotations have been found to be much less efficient for flotation deinking of photocopied office waste.

As indicated in the previous discussion, the fresh photocopying toner ink, which contains more than 85% styrene acrylate copolymer, exhibits a high level of hydrophobicity. In our laboratory, fresh toner was found to be floated almost instantaneously without reagent addition at pH 7. Similar to newsprint paper,<sup>[12]</sup> the cellulose fiber from photocopying paper is extensively hydrated and this hydrophilic property (zero contact angle<sup>[12]</sup>) accounts for its tendency to remain dispersed in suspension. Thus it is expected that an excellent separation of toner ink particles from cellulose fibers should be possible by flotation. However, as described previously, during the photocopying process, the toner ink particles are thermally fused and bonded to the paper and their styrene groups undergo photothermal reactions (oxidation and polymerization) with subsequent formation of peroxide bonds. As a result of the photocopying process the following phenomena occur:

strong bonding of the toner particles with cellulose fibers make the release of toner particle difficult; fusion (polymerization) results in the formation of larger particles of ink, from an initial toner particle diameter of about 10 µm to ink particles of more than 200 µm in diameter;<sup>[49,50]</sup> and oxidation of the surface styrene groups increase the polarity at the toner particle surface. All these characteristics which come from the photocopying process account for the poor efficiency in the flotation deinking of photocopied office wastepaper and need to be considered for the design of improved flotation processes.

## SUMMARY AND CONCLUSION

\* A combined atmospheric thermogravimetry/mass spectrometry system with a low transport resistance interface and low voltage electronic ionization source has been used to study chemical changes in photocopying toner inks during the photocopying process.

\* It has been observed in other experiments that photocopying toner particles, mainly consisting of styrene-acrylate copolymers, exhibit a high level of hydrophobicity prior to printing. However, these particles become more hydrophilic on exposure to heat, light, and oxygen during the printing (copying) process. Surface styrene groups appear to undergo photothermal reactions (oxidation and polymerization) with subsequent formation of peroxide bonds. As a consequence of these photothermal reactions, the thermal decomposition temperatures of the reacted styrene groups increase 10 ~ 30 °C, the corresponding apparent activation energies increase by 7 ~ 20 kcal/mol, and the phase change (softening) of the toner particles at around 72 °C disappears. On the other hand, the acrylate components of the toner are not affected by the photothermal reactions during the photocopying process.

\* It appears that strong bonding of the toner particles with cellulose fibers, polymerization (fusion), and oxidation of the toner result in more hydrophilic and larger ink particles which accounts for the difficulty in making efficient flotation deinking separations in the recycle of photocopied office wastepaper.

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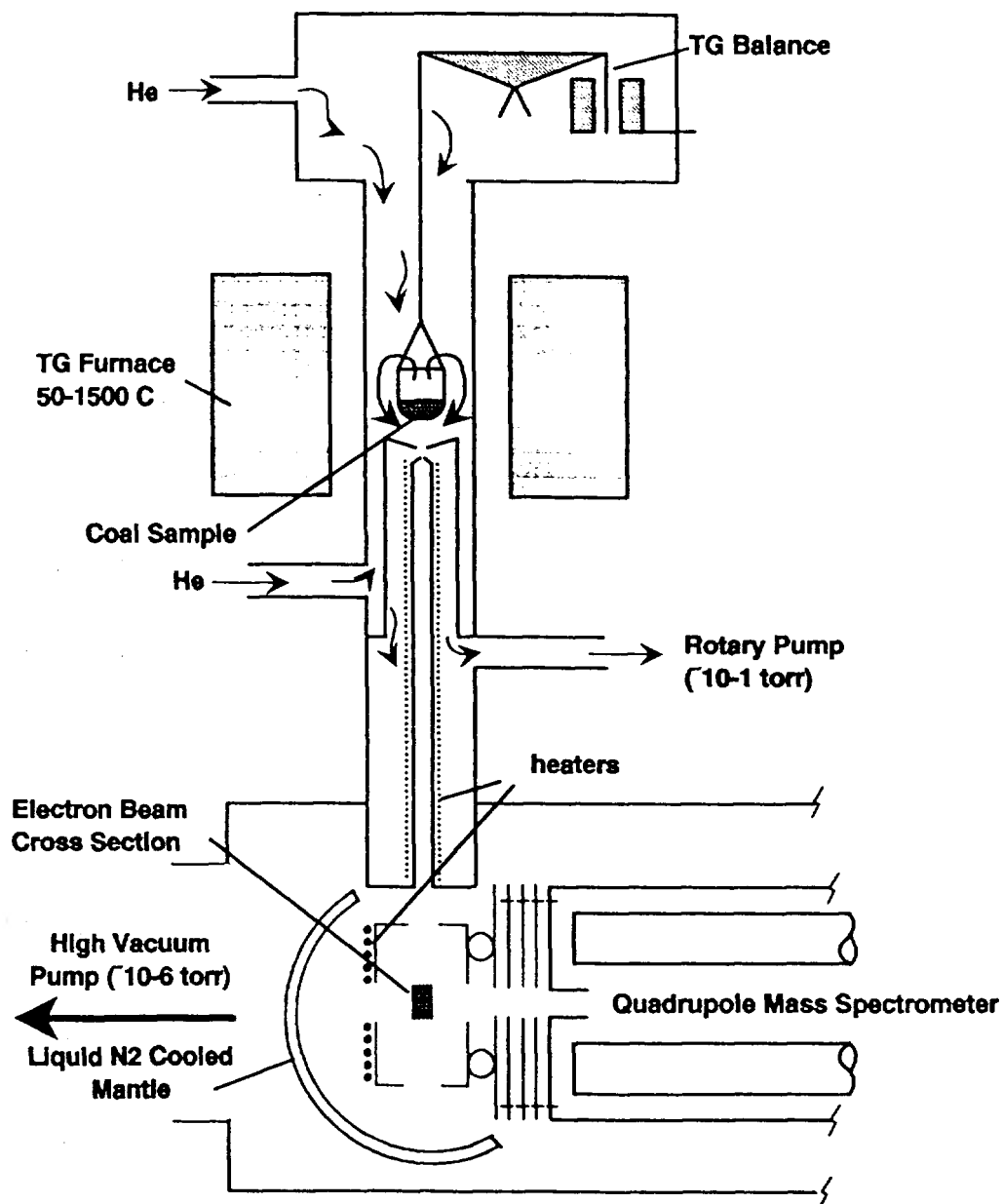
**Table I** Composition of Photocopying Toner Particles

<u>INGREDIENT</u>	<u>CONCENTRATION (%)</u>
Styrene Acrylate	85 ~ 90
Carbon Black	10 ~ 15
Amorphous Silica	< 1
Zinc Stearate	< 1

**Table II** Abundance of  $\alpha$ -methylstyrene and toluene decomposition products relative to methylacrylate

<u>Decomposition Product</u>	<u>FRESH INK</u>	<u>OXIDIZED INK</u>	<u>FUSED INK</u>
$\alpha$ -methylstyrene/ methylacrylate (m/z 118/87)	0.63	0.60	0.37
toluene/methylacrylate (m/z 92/87)	0.19	0.21	0.28





**Fig.1** Schematic diagram of atmospheric thermogravimetry/mass spectrometry system, based on the combination of a Perkin-Elmer TFS-2 microbalance, a Perkin-Elmer 7 series furnace and an Extrel EL 1000 quadrupole mass filter, with a low transport resistance (< 2 seconds of residence time) interface and a low voltage (12 eV) electron-impact ionization source.

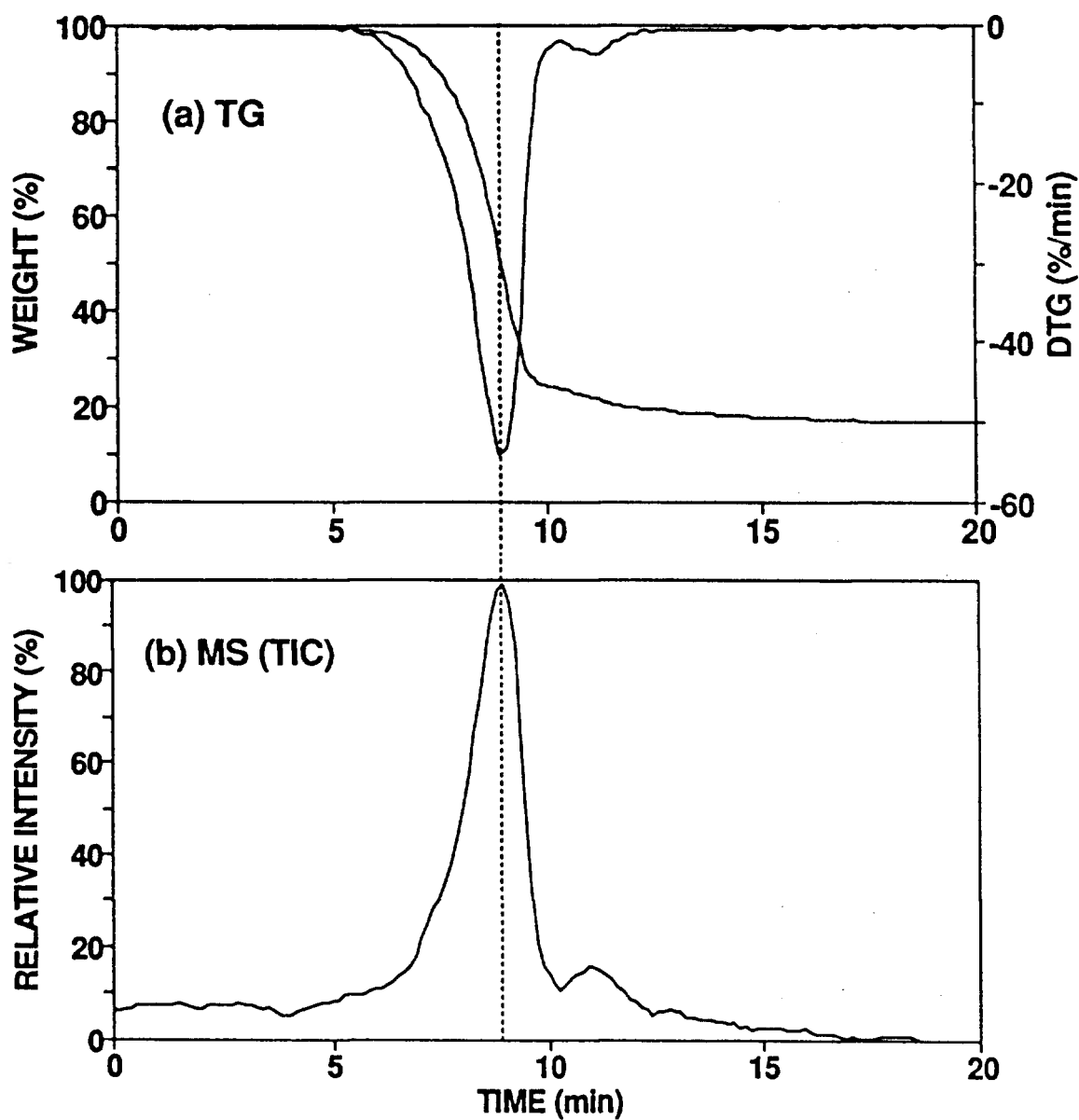


Fig.2 Thermogravimetric (TG), and mass spectrometric total ion chromatogram (TIC) profiles of the photocopied waste paper for a heating rate of 25 °C/min and ambient helium atmosphere.

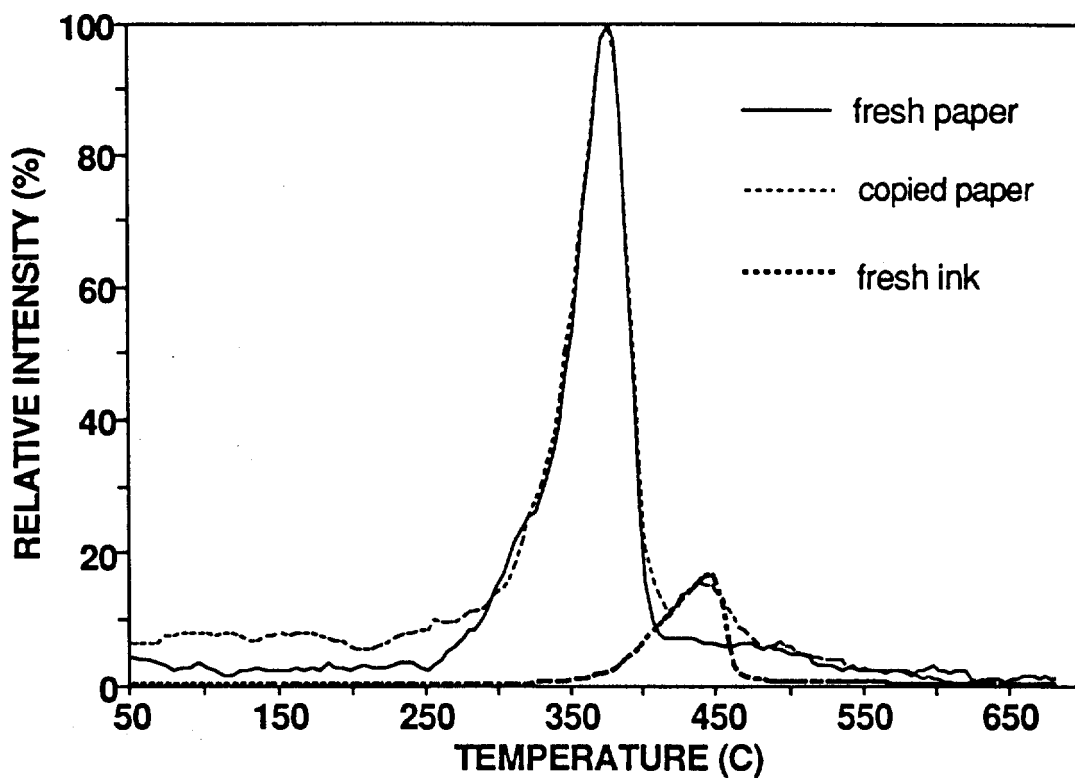


Fig.3 The mass spectrometric total ion chromatogram (TIC) profiles of photocopying toner inks for a heating rate of 25 °C/min.

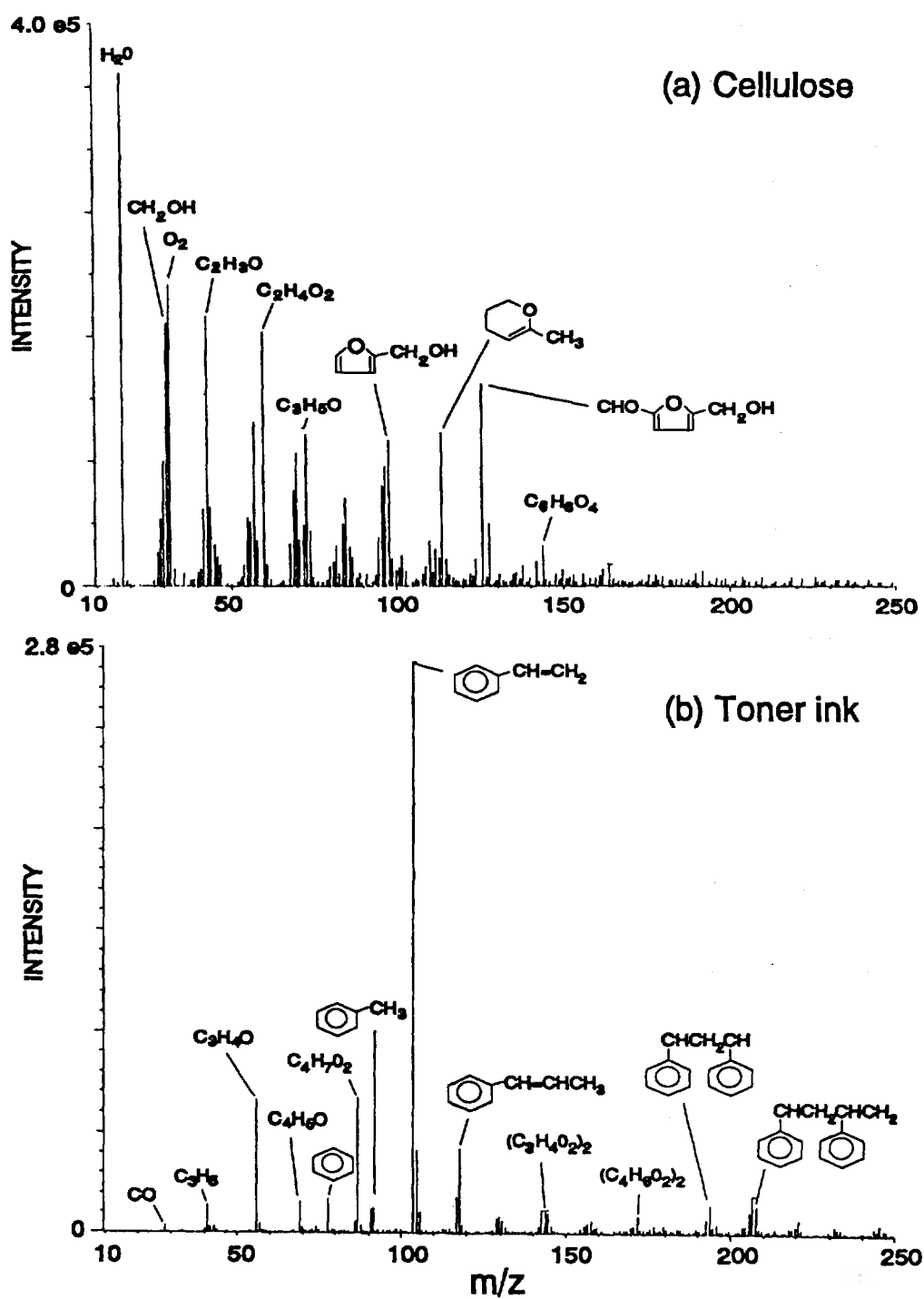


Fig.4 Time-integrated spectra by summing all evaporation spectra scanned during TG/MS runs for cellulose and photocopying toner ink.

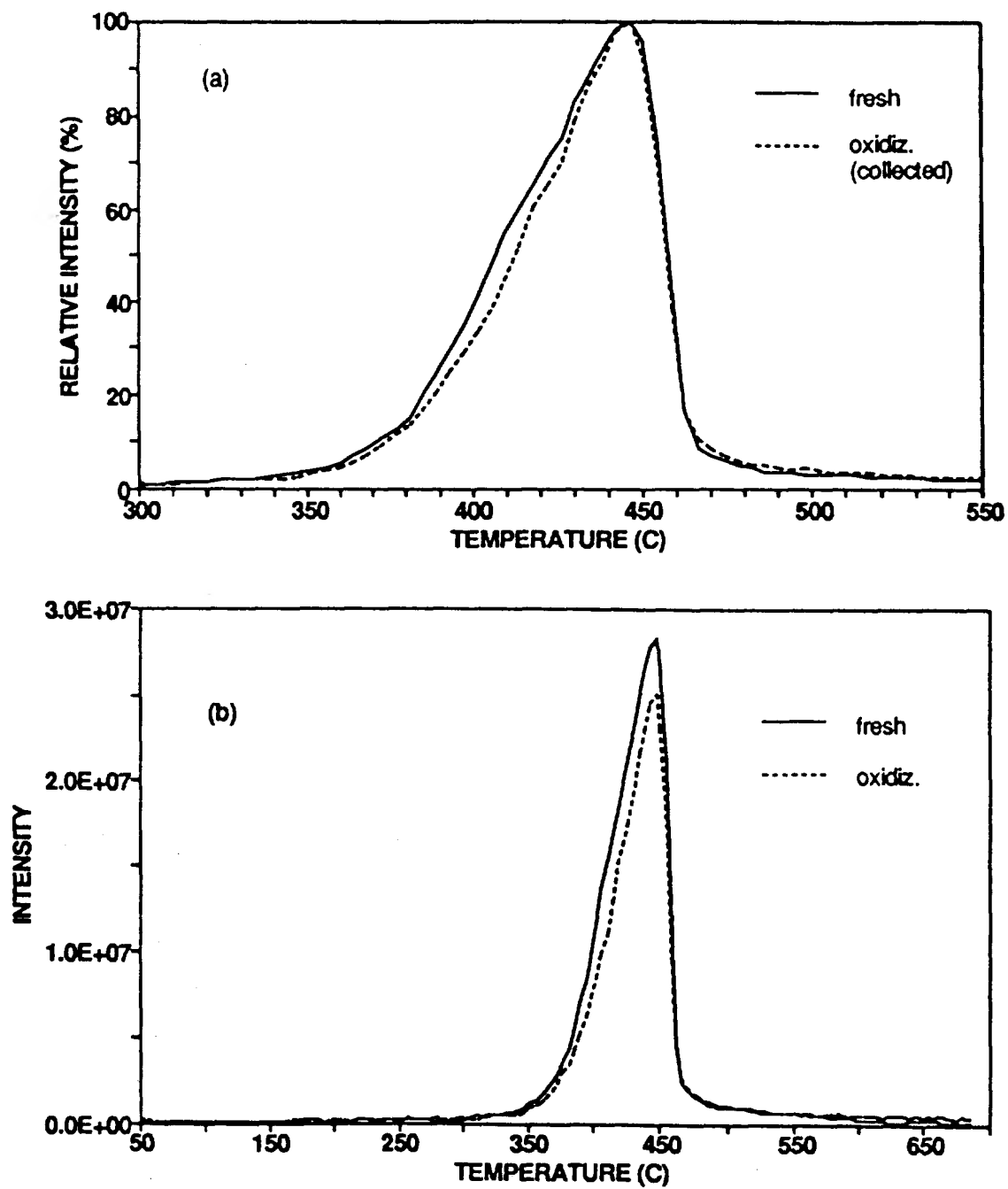


Fig.5 The mass spectrometric total ion chromatogram (TIC) profiles of fresh toner ink and the oxidized ink collected in the photocopying machine's waste bottle for both the relative and absolute intensity scales.

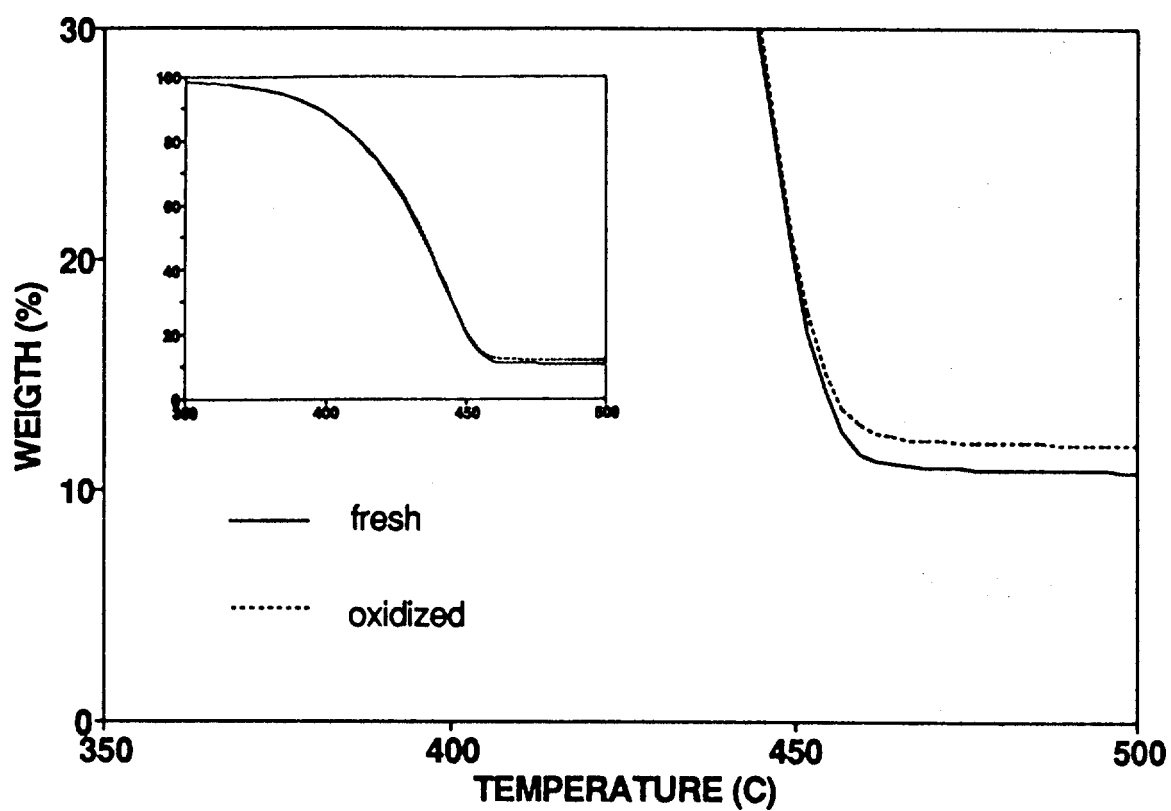


Fig.6 Thermogravimetric profiles of fresh toner ink and the oxidized toner ink collected in photocopying machine's waste bottle.

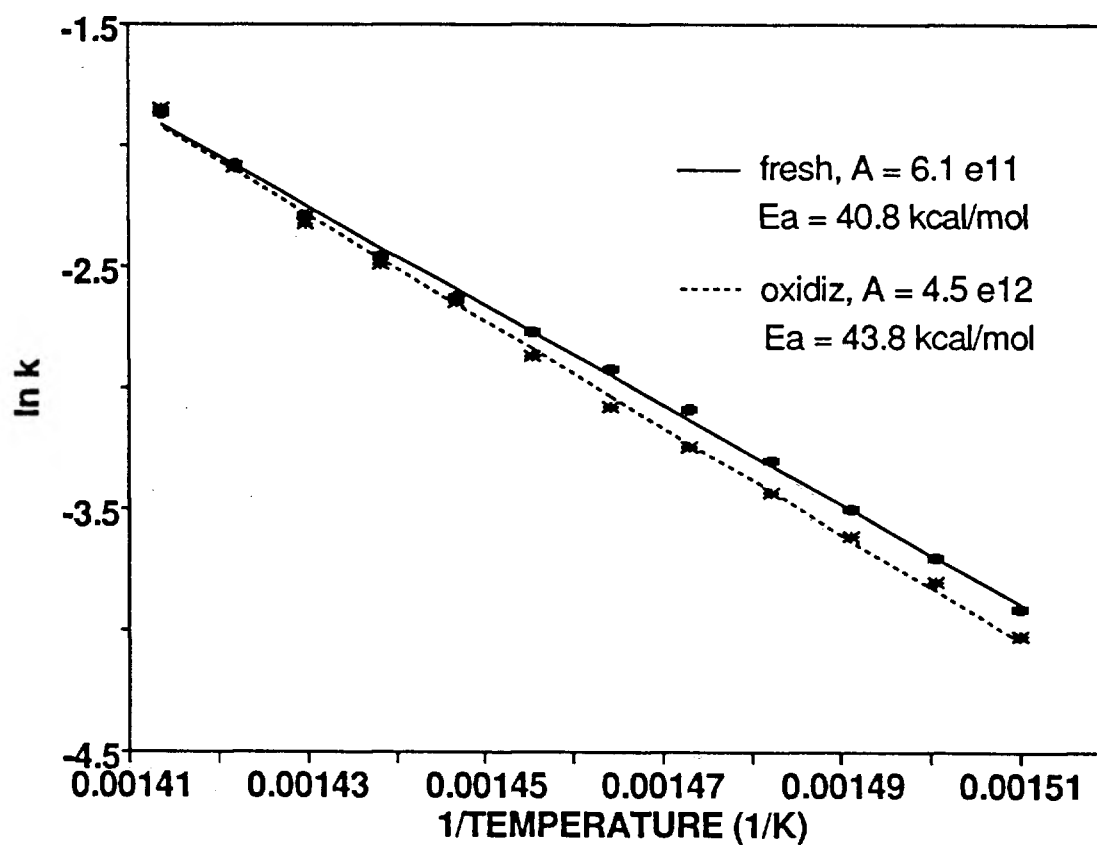


Fig.7 Plot of the rate constants calculated for the mass spectrometric total ion chromatogram of fresh toner ink and the oxidized toner ink collected in the photocopying machine's waste bottle vs. reciprocal temperature.

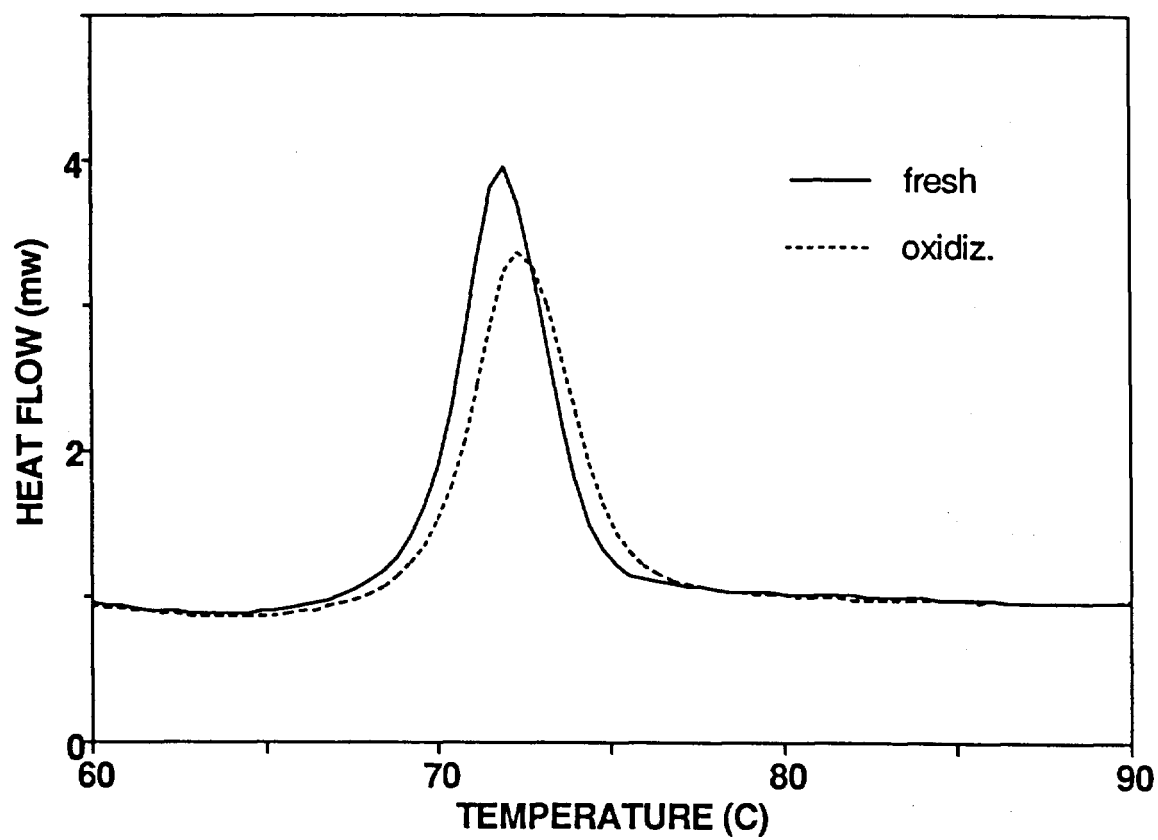


Fig.8 Differential scanning calorimeter profiles of fresh toner ink and the oxidized toner ink collected in the photocopying machine's waste bottle.



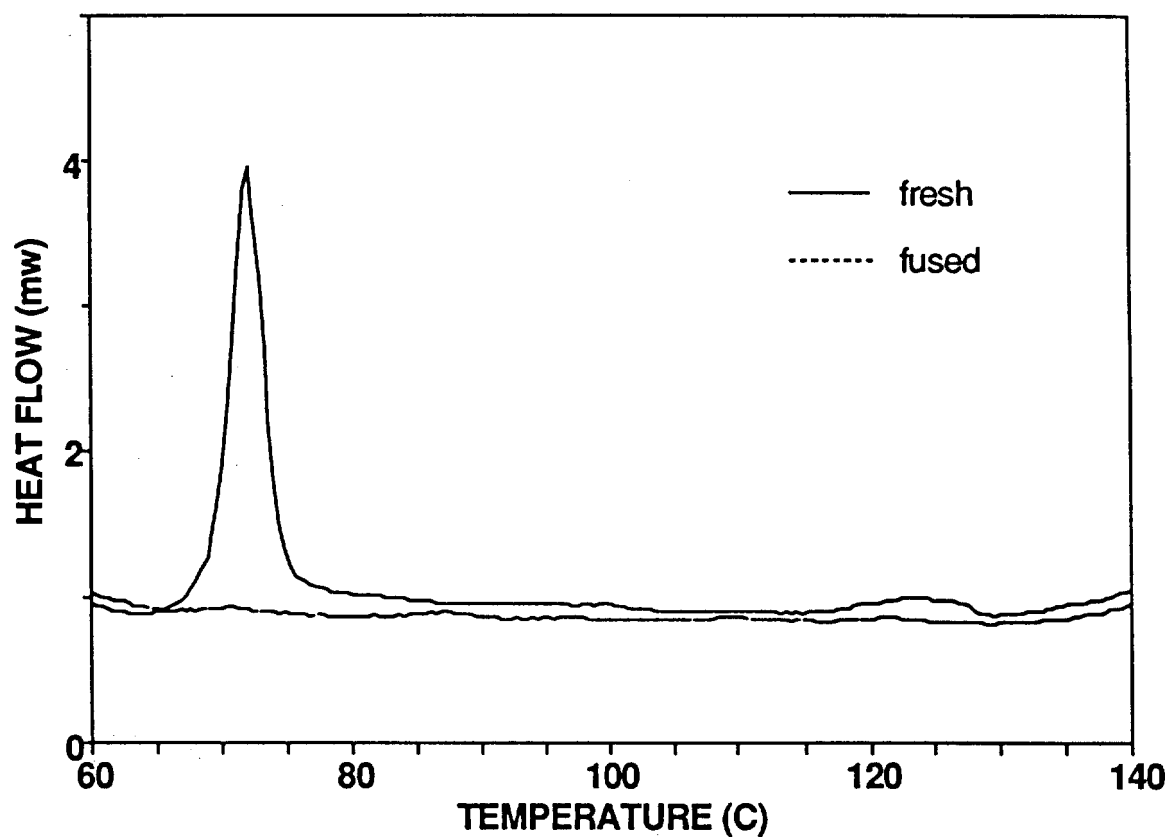


Fig.9 Differential scanning calorimeter profiles of the (fresh) toner ink, which was run at first time, and the (fused) toner ink, which was rerun at second time.

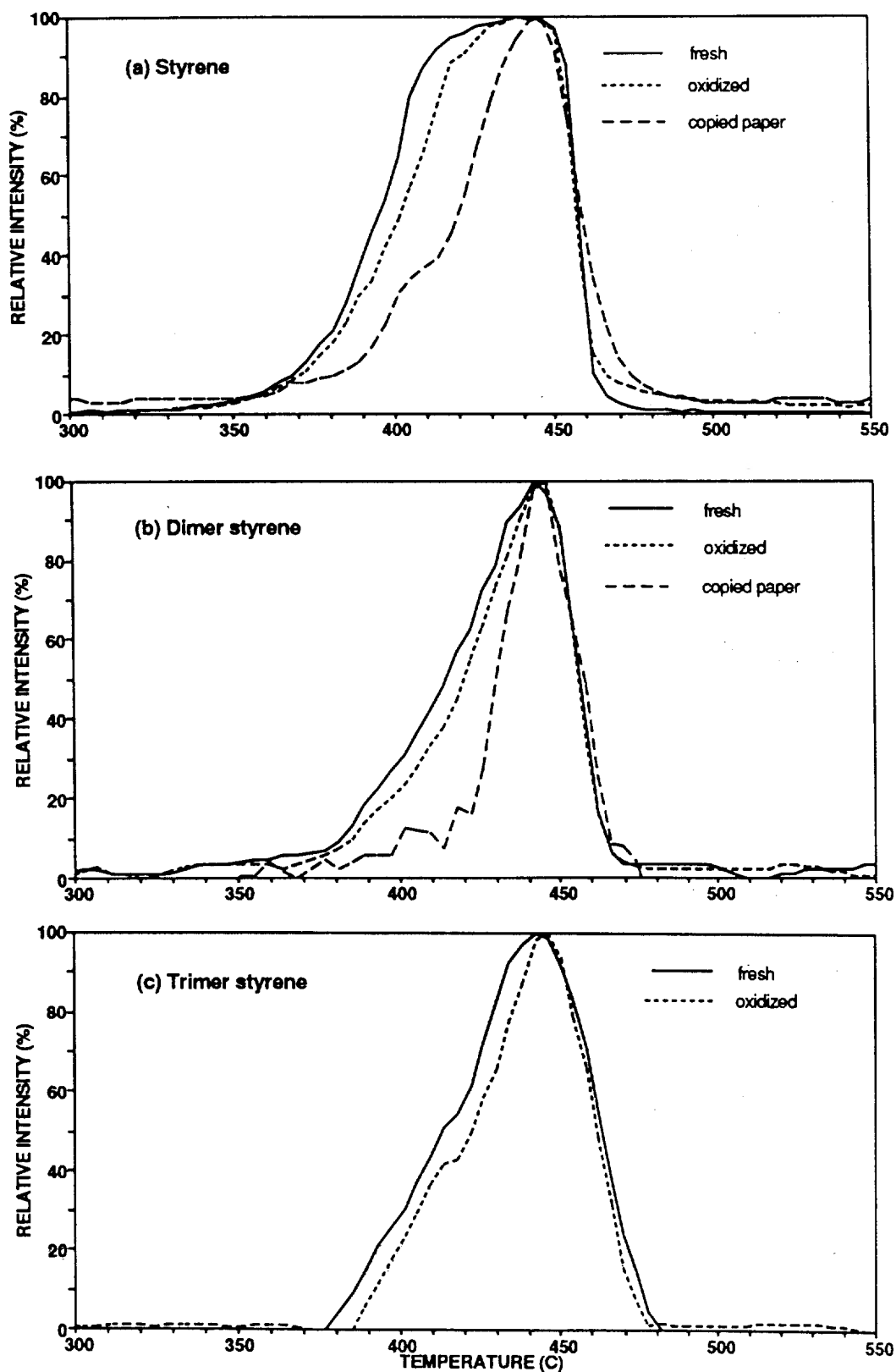


Fig.10 The mass spectrometric selected ion chromatogram (SIC) profiles of (a) monomer styrene ( $m/z104$ ), (b) dimer styrene ( $m/z207$ ), and (c) trimer styrene ( $m/z312$ ) of toner inks.

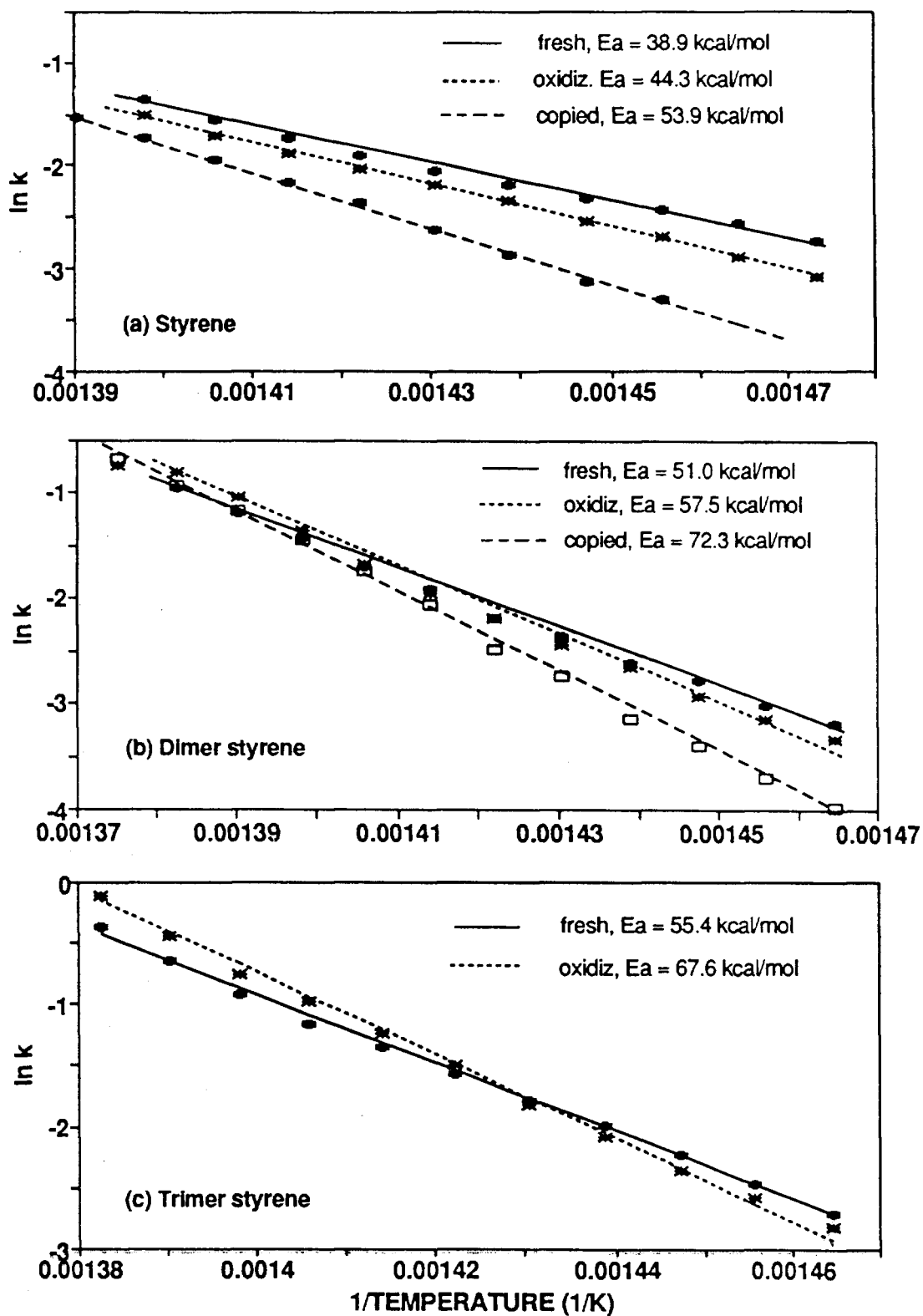


Fig.11 Plot of the rate constants calculated from the mass spectrometric selected ion chromatogram of (a) monomer styrene ( $m/z104$ ), (b) dimer styrene ( $m/z207$ ), and (c) trimer styrene ( $m/z312$ ) of toner inks vs. reciprocal temperature.

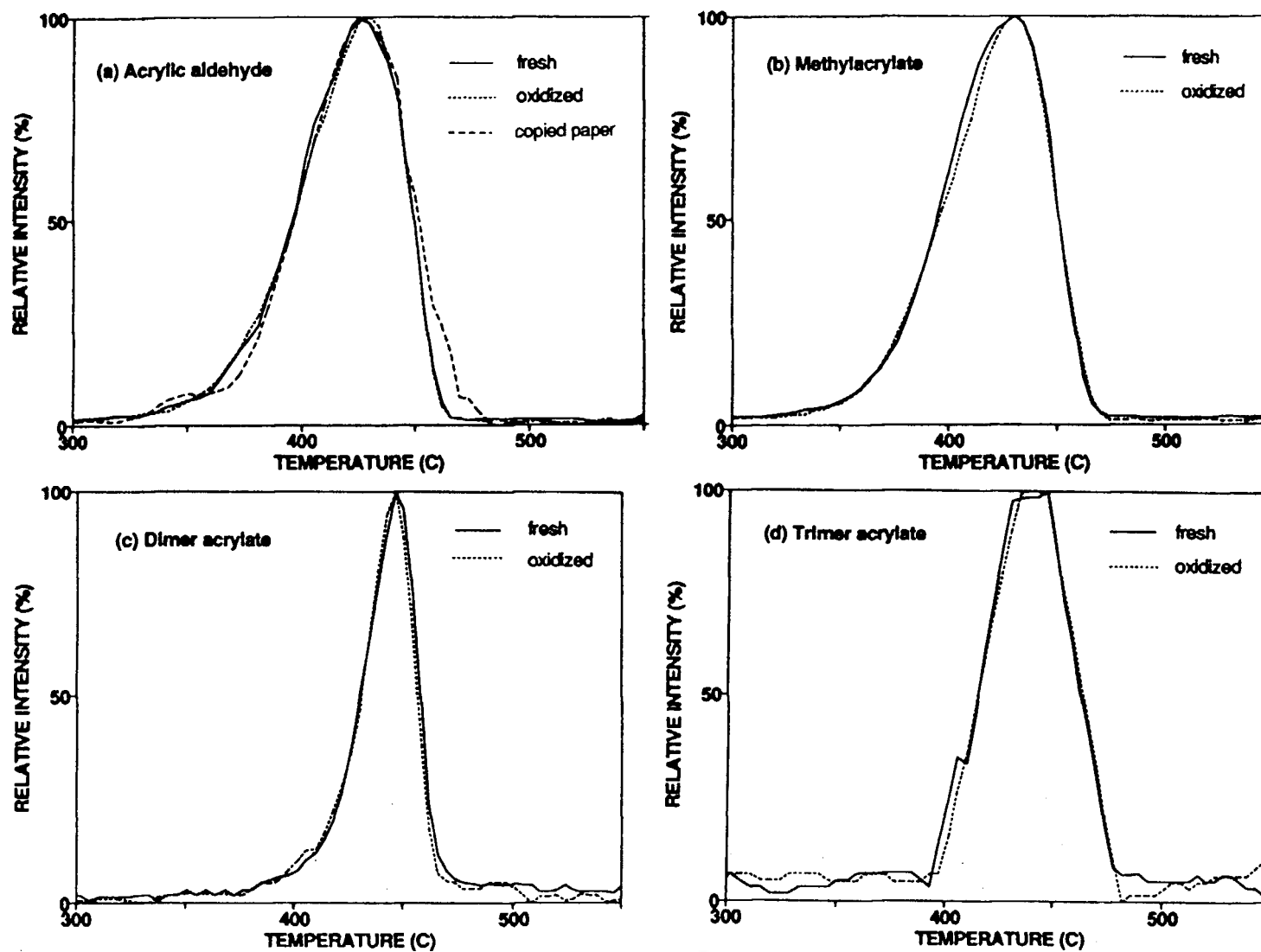


Fig.12 The mass spectrometric selected ion chromatogram (SIC) profiles of (a) acrylic aldehyde ( $m/z56$ ), (b) methylacrylate ( $m/z87$ ), (c) dimer acrylate ( $m/z144$ ), and (d) trimer acrylate ( $m/z216$ ).

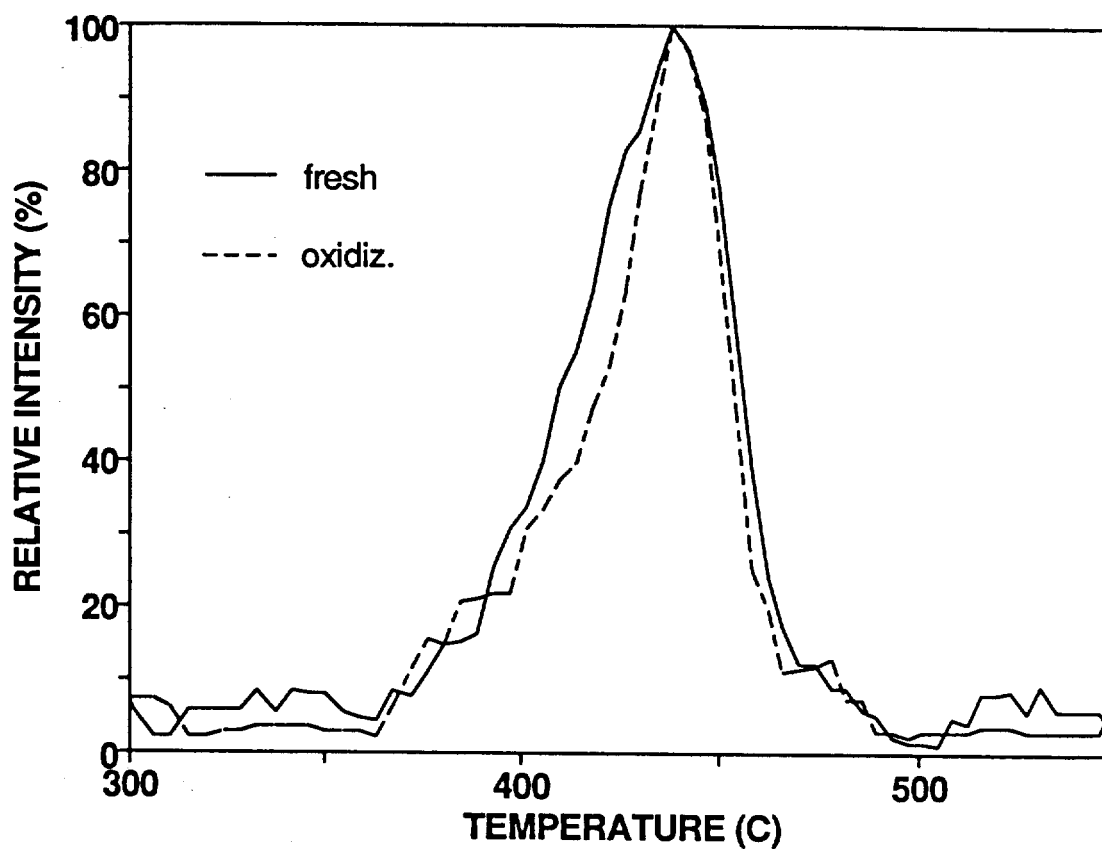


Fig.13 The mass spectrometric selected ion chromatogram (SIC) profiles of the styrene-acrylate ( $m/z$ 177) from toner inks

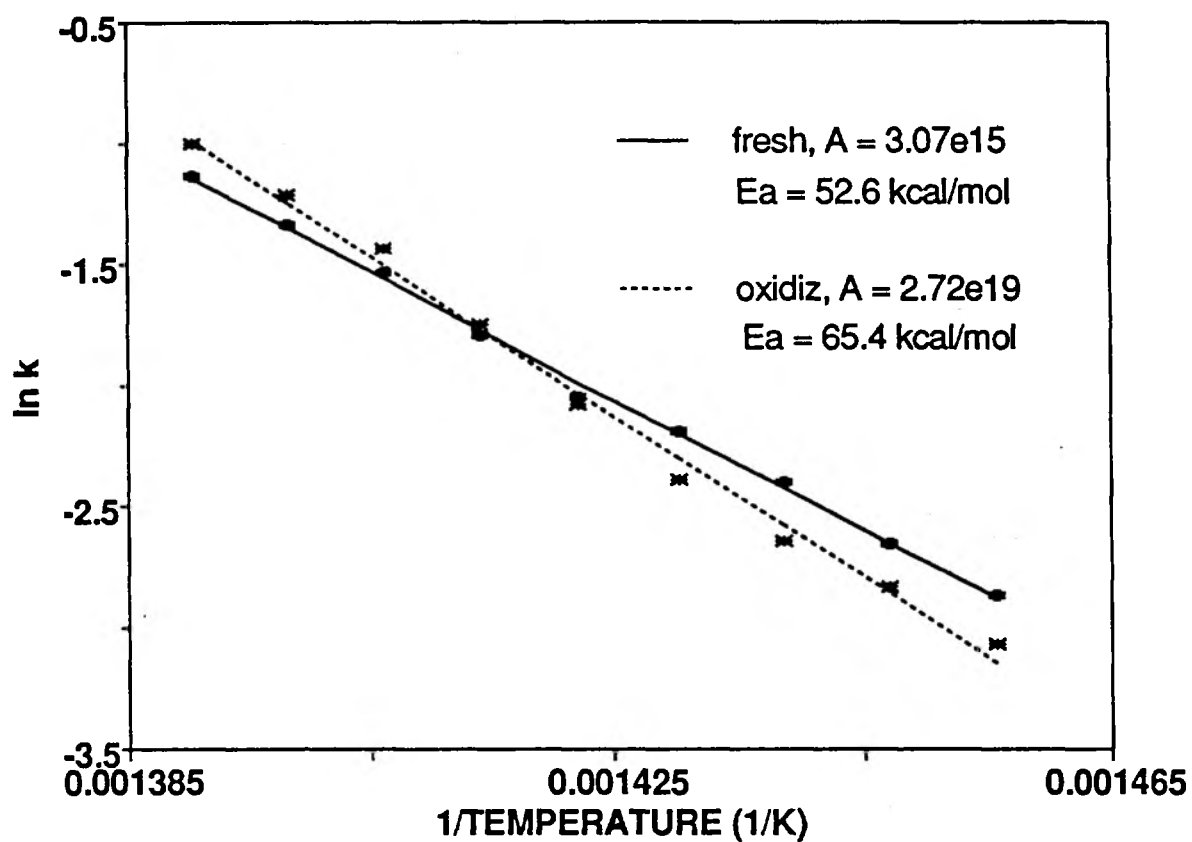


Fig.14 The plot of the rate constants calculated by the mass spectrometric selected ion chromatogram of styrene-acrylate from toner inks vs. reciprocal temperature.

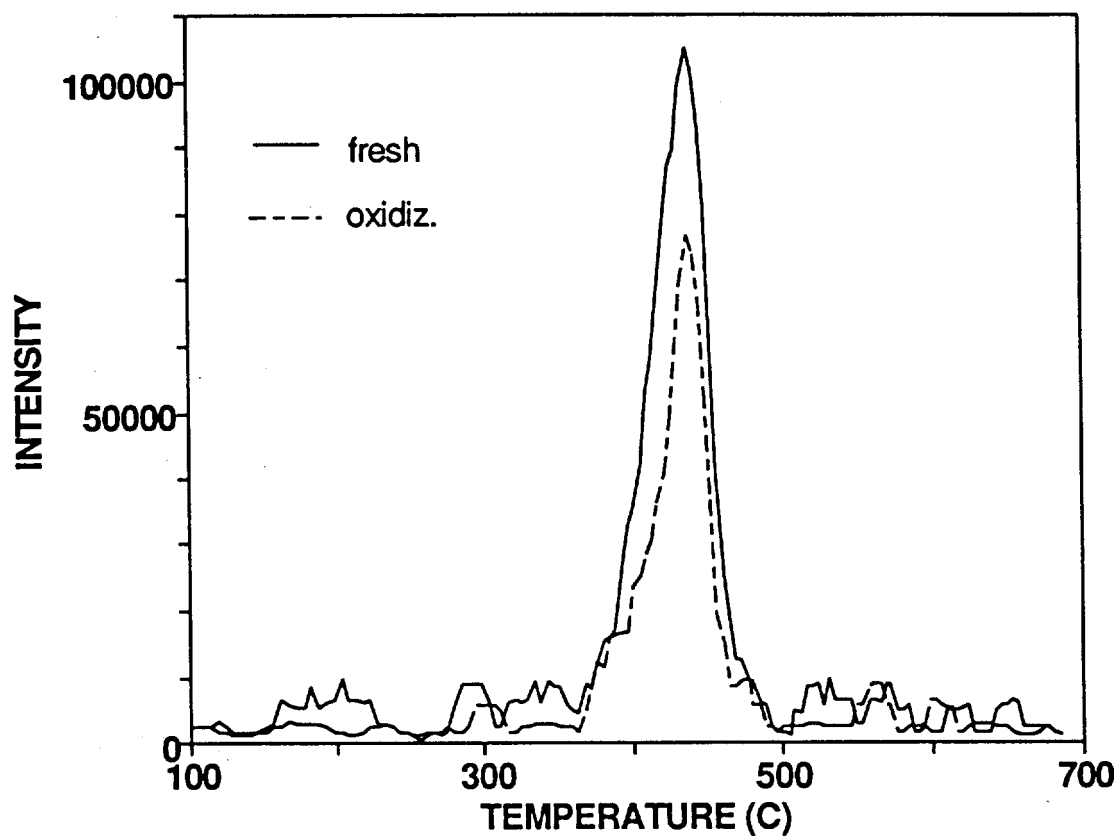


Fig.15 The mass spectrometric selected ion chromatogram (SIC) profiles of styrene-acrylate (m/z177) from toner inks on the absolute scale

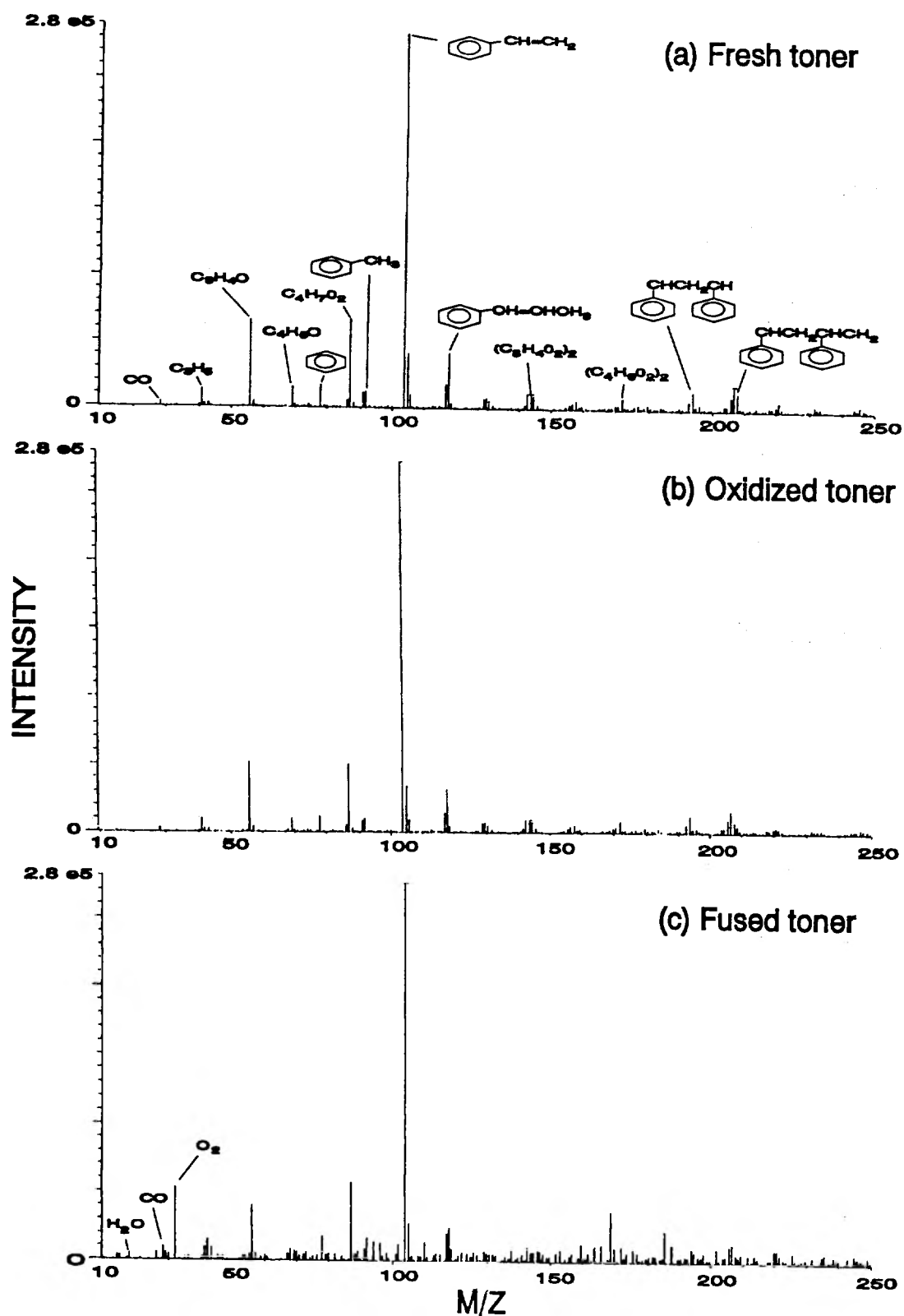


Fig.16 Time-integrated spectrum by summing all evaporation spectra scanned during TG/MS runs for fresh, oxidized and fused toner inks.